

themselves*, and on the alleged destruction of germs by merely drying them, on hermetic sealing, and on the deportment of hermetically sealed flasks exposed to the sun of the Alps, are introduced towards the end of the memoir.

Throughout these laborious researches I have been aided, with his accustomed zeal and ability, by my excellent senior assistant, Mr. John Cottrell. He has been worthily seconded by Mr. Frank Valter, and, in an humbler but still effectual way, by William Card.

May 31, 1877.

Dr. J. DALTON HOOKER, C.B., President, in the Chair.

The Presents received were laid on the table, and thanks ordered for them.

The following Papers were read :—

- I. “The Physical Properties of Homologues and Isomers.” By FREDERICK D. BROWN, B.Sc. Communicated by HENRY E. ARMSTRONG, Ph.D., F.R.S., Sec. C.S., Professor of Chemistry in the London Institution. Received April 23, 1877.

Observations of the physical properties of chemical compounds have been very numerous ; in many, however, the object aimed at has been merely the definition of the substances in question, and the results lay claim to no great accuracy. In others, data have been required for the solution of purely physical problems, and but little attention has been paid to the chemical nature of the substances employed. In comparatively few has equal importance been attached to both the physical and chemical aspects of the question.

If, then, we attempt to compare the physical properties of a series of compounds presenting very similar chemical properties, we find that in the case of one or two members of the series our knowledge is tolerably

* By the excellent researches of Dallinger and Drysdale it has been proved that the germs of Monads, as compared with the adult organisms, possess a power of resistance to heat in the proportion of 11 to 6.

complete, but that with regard to the others little is known but their approximate boiling-points and densities.

Among the alcohols of the $C_nH_{(2n+1)} \cdot OH$ series, for example, there are two (methyl and ethyl alcohols) with whose physical properties we are well acquainted. The expansion of these bodies has been determined by Kopp, Pierre, Mendelejeff, and others; the vapour-tensions, latent and specific heats by Regnault; the latent heat by Andrews also; the refractive indices by Gladstone and Dale. Nearly all these researches, and many more which might be enumerated, have been accompanied by measurements of density and boiling-point.

When we pass to the other members of the series we find, however, that in the case of normal propyl alcohol, with the exception of numerous determinations of density and boiling-point, experiments have been limited, as far as I am aware, to the measurement of the expansion by Pierre and Puchot. (The table of vapour-tensions given in the same paper is erroneous, as I hope to prove in a future communication.) The same is to be said of all the other alcohols of this series, the rates of expansion of some of which have been examined by Kopp, Lieben and Rossi, Wanklyn and Erlenmeyer, and others.

In order partially to supply this want I have undertaken a series of experiments, of which the following pages are the firstfruits.

I. Density, Expansion, and Vapour-tension of Propyl and Isopropyl Iodides.

The selection of these as my first experiments was prompted by the following considerations:—If, as is possible, all the particular physical characteristics of a given substance result from one main characteristic, which is, as it were, the fundamental definition of the substance (at least from a physical point of view), then the various phenomena observed must be dependent one on the other, and the measurement of the vapour-tension, for instance, or of the latent heat, of the given substance must involve implicitly all other measurements, such as those of the specific heat, rate of expansion, &c.; that this is not without foundation, is proved by the many partially successful attempts to connect the various results obtained for certain bodies by mathematical reasoning.

A connexion between the vapour-tension and rate of expansion of a liquid organic body is rendered probable by the well-known researches of Hermann Kopp and others. From a large number of observations conclusions were formed which may be thus summed up:—The atoms of the various elements entering into the composition of substances of the same chemical type always occupy the same space when the tension of the vapour of the liquid is equal to the pressure exerted by a column of mercury 760 millims. in height. Hence the molecules of isomeric sub-

stances which differ only in the arrangement of their constituent atoms, and not in their number or kind, must, when the tension equals 760 millims., occupy the same space, or, in other words, the molecular volumes of isomers at their boiling-points are equal. If this relation exists between the molecular volumes of two isomers at those temperatures at which their respective vapour-tensions are equal to 760 millims., it should equally hold good at all those corresponding temperatures at which the vapour-tensions are equal to any number n of millimetres, since the ordinary barometric pressure of 760 millims. is a special circumstance due to our residence on this planet and to the usual position of our laboratories at no great altitude.

The study of the vapour-tensions, combined with that of the density and rate of expansion, enables us therefore to compare the molecular volumes at all those corresponding temperatures at which the vapour-tensions are equal; should a uniform equality be apparent, it is evident that a connexion between vapour-tension and rate of expansion would be established. For, let A and a be two isomeric liquids, D and d their respective densities, and H and h their vapour-tensions at any temperature t , we have $D=f(t)$, $d=f'(t)$, $H=\phi(t)$, $h=\phi'(t)$; if we have observed that whenever $H=h$ $D=d^*$, it of course follows that for any two values t_1 and t_2 such that $\phi(t_1)=\phi'(t_2)$ we shall have also $f(t_1)=f'(t_2)$.

Since the expressions $\phi(t)$ and $f(t)$ present no peculiarities in the case of isomeric substances, it would be reasonable to suppose that in the case of other liquids there is also a relation between $\phi(t)$ and $f(t)$.

A detailed description of the apparatus employed, together with all the precautions taken to ensure accuracy, must be reserved for the future; a brief statement on this head is, however, indispensable.

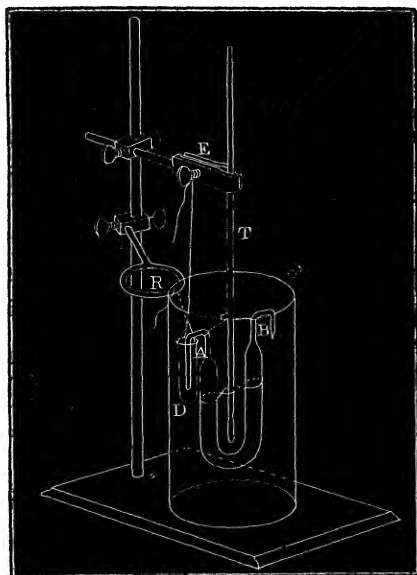
Thermometers.—The two thermometers by which all measurements of temperature were taken are each about 20 inches long, and are divided on the glass into tenths of a degree; the scale of the one (A) ranges from -7° to 53° , that of the other (B) from 46° to 102° . These instruments were most carefully compared with a Kew standard which has long been in the possession of the London Institution.

The bath in which the comparisons were made was 22 inches in height and 12 inches in breadth, and was filled with water which was rapidly and constantly stirred; the readings were marked on paper divided carefully into squares, and the points united by a curved line; the corresponding readings of the air thermometer derived from Regnault's Tables being also marked, the correction for any subse-

* V and v being the respective molecular volumes, and m the common molecular weight, we have $V=\frac{m}{D}$ and $v=\frac{m}{d}$; consequently when $V=v$, $D=d$: we may therefore substitute the equality of the densities for that of the molecular volumes.

quent reading of either of the instruments could be obtained by direct measurement.

Fig. 1.



The error of observation of the temperatures is never greater than $0^{\circ}.02$.

Determination of Densities.—The capillary ends of a U-tube of Dr. Sprengel's pattern, the capacity of which is about 14 cub. centims., were bent down as at A and B; when the tube had been filled with the liquid, and fastened to the thermometer in the position shown in fig. 1, a small tube D, containing a little of the liquid, was suspended so that the end A plunged into it; the tube was then completely filled by sucking with an india-rubber tube at B, and lowered into a large beaker of water, the temperature of which was slightly above that of the room; after stirring frequently for about 15 minutes, the thread supporting the tube D was removed from the clamp E to a fixed ring R. The temperature having been read, the clamp E was finally raised, carrying with it the density-tube completely full. On exposure to the cooler air the liquid in the capillaries quickly recedes, and the tube may be wiped dry and weighed.

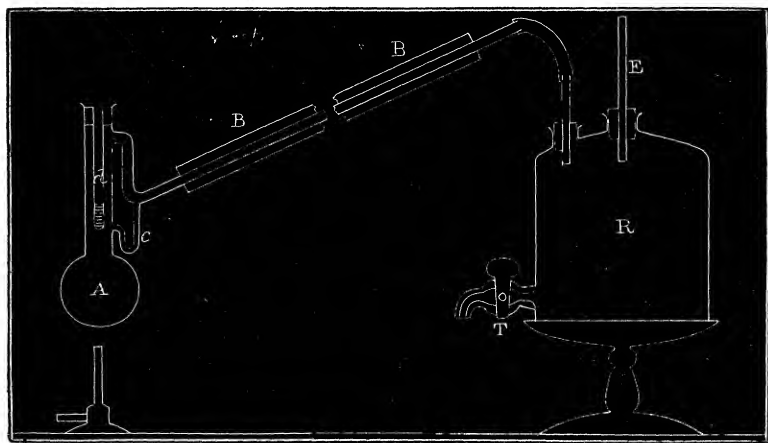
This slight modification of the ordinary method enabled me to determine easily the density of a liquid at any temperature above that of the atmosphere, however great might be the rate of expansion. The tube being completely full, the error which in general arises from the adherence of the liquid to empty portions of density-tubes &c. is avoided. The

densities are referred to water at zero; the error of the observations is less than 0.00005.

Rate of Expansion.—Dilatometers, similar to those used by Kopp, Pierre, and others, were employed, the necessary data concerning them being obtained in the usual way, slight modifications excepted. The instruments, when filled with the liquid to be examined, were compared with the thermometers A and B, in the large bath mentioned above, in which they were completely immersed; readings were taken both when the temperature of the water was rising and when it was falling. When both dilatometers were filled with the same liquid, the volumes obtained at any given temperature differed only in the fifth decimal place.

Vapour-tension.—The apparatus shown in fig. 2 was used in the case of the iodides. The vapour of the liquid boiling in the bulb A condenses in the tube BB and runs back by the small tube c; any cooling of the thermometer by the condensed vapour is thus avoided. R is a reservoir of air with a tap T, with which an air-pump is connected, while the tube E is connected with a pressure-gauge formed of two communicating columns of mercury. The thermometer is placed in the tube d, which is closed at the bottom and contains a little mercury.

Fig. 2.



A liquid which is not decomposed by heat below its boiling-point will boil in this apparatus at any temperature and for any length of time, without the thermometer varying one hundredth of a degree. About 100 cub. centims. of the liquid were put in the bulb.

Normal Propyl Iodide.—This substance was prepared by treating pure propyl alcohol with hydriodic-acid gas; the saturated liquid was distilled with steam, the distillate shaken several times with a weak solution of caustic soda, a little iodine added to destroy the phosphorus compounds, again shaken with soda, then with water, and finally dried with phosphoric

anhydride. The pure iodide thus obtained amounted to about 1100 grms.; it was carefully fractioned, and after four distillations collected in the following five portions :—

A. Below 102°.	} Temperatures not corrected.
I. 102°·0 to 102°·25.	
II. 102°·25 to 102°·5.	
III. 102°·5 to 102°·75.	
B. Above 102°·75.	

The densities of I., II., and III. were as follows :—

I. 1·74772 at 20°·79 ; 1·78684 at 0°.
II. 1·75035 at 19·27 ; 1·78641 at 0.
III. 1·74628 at 20·91 ; 1·78550 at 0.

The densities at zero are calculated by means of the curve of expansion afterwards determined.

For the mean density of zero we have $D=1·7863$.

The density is given by Chapman and Smith (*Chem. Soc. Journ.* xxii. 195) as 1·7343 at 16°; by Rossi (*Ann. Chem. und Pharm.* clix. 79) as 1·782 at 0°; by Linnemann (*Ann. Chem. und Pharm.* clxi. 34) as 1·7610 at 16°; and by Pierre and Puchot (*Ann. Chim. et Phys.* (4) xxii. 286) as 1·7842 at 0°.

To obtain the rate of expansion, one of the dilatometers was filled with Fraction I. and another with III. The final results were as follows:—

FRACTION I.			FRACTION III.		
No. of Obs.	Temperature (corrected).	Volume.	No. of Obs.	Temperature (corrected).	Volume.
1	0° (ice)	1·00000	2	0° (ice)	1·00000
3	7·06	1·00745	3	7·08	1·00740
3	15·01	1·01601	3	15·07	1·01606
3	23·95	1·02586	3	23·99	1·02593
3	30·99	1·03383	3	31·00	1·03385
2	39·01	1·04312	4	39·09	1·04322
3	44·23	1·04933	3	44·20	1·04930
4	50·41	1·05655	5	50·35	1·05644
3	50·56	1·05672	3	50·45	1·05655
3	57·16	1·06501	3	57·06	1·06479
3	68·07	1·07895	3	67·84	1·07849
3	75·21	1·08830	3	75·11	1·08797
3	80·87	1·09600	3	80·77	1·09558
3	88·70	1·10671	3	88·58	1·10603
5	96·94	1·11836	5	96·74	1·11750

The above results were marked on a large sheet of paper divided by parallel lines into squares, and the points united by means of a curve; the two curves thus obtained being nearly coincident, I judged it unnecessary to repeat the experiment with Fraction II.

The following Table gives the volume of Fraction III. at every ten degrees from 0° to 100°; these numbers are measured direct from the curve, and represent the experiments quite as well as if calculated by means of an equation of the formula

$$V=1+at+\beta t^2+\gamma t^3.$$

Temperature.	Volume as measured from curves.	Volume given by Pierre.	Temperature.	Volume as measured from curves.	Volume given by Pierre.
0	1.00000	1.000	60	1.06852	1.069
10	1.01052	1.010	70	1.08128	1.082
20	1.02142	1.021	80	1.09446	1.096
30	1.03274	1.0324	90	1.10802	1.1105
40	1.04436	1.044	100	1.12200	1.125
50	1.05600	1.056	104.5	...	1.132

The difference between the numbers at the higher temperatures is doubtless partly due to the fact that Pierre measured the density at only four temperatures, viz. 0°, 9°·1, 52°·6, and 75°·3, and then calculated the above series of numbers by means of a formula of interpolation; it will be observed that a small error in the determination of the density at 75°·3 would be sufficient to cause the discrepancy referred to.

The vapour-tension of the normal iodide was determined by boiling in the apparatus described above; here, again, Fractions I. and III. only were employed. The following Table gives the results obtained: the observations marked thus * were made with platinum foil in the boiling liquid; with the others this was not the case.

FRACTION I.			FRACTION II.		
No. of Obs.	Boiling-point.	Pressure in millims.	No. of Obs.	Boiling-point.	Pressure in millims.
3	52.66	138.9	2	53.06	138.6
2	59.86	184.7	1	53.17	139.8*
1	62.95	208.0	1	53.26	139.6
1	72.12	289.9	1	56.17	157.9*
1	83.32	424.9	3	61.80	195.9
1	93.85	591.9	1	62.70	203.0*
1	101.14	735.0	1	70.45	269.6
1	102.00	753.4	1	79.11	365.3
			1	84.15	431.3*
			1	90.05	520.0
			1	96.81	640.4
			1	100.21	707.1
			1	100.45	712.7*
			1	101.37	732.1

I attempted to measure the vapour-tensions of this substance in an apparatus similar to that now used for the analysis of gases, one of the vertical tubes, however, being heated in a large quantity of water, which was made to circulate by means of a screw. This apparatus (which will be described on another occasion) answers perfectly in the case of most substances, but both the iodides now under consideration are decomposed by the mercury; the normal iodide, however, being but slowly acted upon in the cold, I was able to measure the vapour-tension several times at about 7°. The mean result shows a tension of 15·4 millims. at 7°·5.

The curves constructed by means of the above data diverge gradually until at a tension of 760 millims., the corresponding temperatures differing

by 0°·5. The equation $H = ab^{\frac{t}{1+mt}}$ (where H = the tension of the vapour, t = the temperature in degrees Centigrade $+ 7^{\circ} \cdot 5$) expresses the observations for Fraction III. with great exactitude when

$$\log a = 1 \cdot 1875207,$$

$$\log b = 0 \cdot 0259870,$$

$$\log m = 3 \cdot 6338070.$$

Isopropyl Iodide.—This body was prepared by heating glycerin with iodine and phosphorus, and purifying as in the case of the normal iodide; more than a kilogramme of the pure substance was obtained. After fractional distillation three portions were obtained boiling as follows :—

$$\left. \begin{array}{l} \text{I. } 88^{\circ} \cdot 6 \text{ to } 88^{\circ} \cdot 7 \\ \text{II. } 88^{\circ} \cdot 7 \text{ to } 88^{\circ} \cdot 8 \\ \text{III. } 88^{\circ} \cdot 8 \text{ to } 89^{\circ} \cdot 0 \end{array} \right\} \begin{array}{l} \text{Temperatures} \\ \text{uncorrected.} \end{array}$$

The densities of these three fractions were as follows :—

$$\begin{array}{l} \text{I. } 1 \cdot 70526 \text{ at } 19^{\circ} \cdot 80; 1 \cdot 74315 \text{ at } 0 \\ \text{II. } 1 \cdot 70506 \text{ at } 20 \cdot 14; 1 \cdot 74363 \text{ at } 0 \\ \text{III. } 1 \cdot 70457 \text{ at } 21 \cdot 09; 1 \cdot 74504 \text{ at } 0. \end{array}$$

The mean density at 0° is therefore

$$D = 1 \cdot 7440.$$

The density of isopropyl iodide is given by Erlenmeyer (Ann. Chem. Pharm. cxxvi. 309) as 1·714 at 16°; by Linnemann (Ann. Chem. Pharm. cxxxix. 229) as 1·735 at 0°; by Buff (Ann. Chem. Pharm. Supp. iv. 129) as 1·71732 at 17°.

The observations on the expansion were as follows :—

FRACTION II.			FRACTION III.		
No. of Obs.	Temperature (corrected).	Volume.	No. of Obs.	Temperature (corrected).	Volume.
1	0°0 (ice)	1·00000	1	0°0 (ice)	1·00000
3	14·79	1·01653	1	11·28	1·01263
3	25·81	1·02933	2	15·58	1·01751
2	35·61	1·04110	2	21·84	1·02475
2	39·51	1·04587	2	27·78	1·03178
3	52·28	1·06200	2	32·64	1·03756
3	57·88	1·06947	3	46·97	1·05513
3	70·14	1·08633	3	55·22	1·06591
			3	63·16	1·07662
			3	71·87	1·08865
			4	79·66	1·09994

The two curves drawn by means of these data coincided throughout. The volumes at every ten degrees are as follows :—

Temperature.	Volume.	Temperature.	Volume.	Temperature.	Volume.
0	1·00000	40	1·04640	70	1·08606
10	1·01118	50	1·05900	80	1·10032
20	1·02246	60	1·07234	90	1·11480
30	1·03440				

The following are the results obtained when these two fractions were boiled at various pressures :—

FRACTION II.			FRACTION III.		
No. of Obs.	Boiling-point.	Pressure in millims.	No. of Obs.	Boiling-point.	Pressure in millims.
1	49°32	191·9	2	48°90	187·9
1	52·15	214·3	1	54·43	232·6
2	59·45	281·3	3	55·93	245·9
2	69·55	400·3	3	62·40	311·2
1	73·46	455·6	1	69·63	399·7
1	76·21	498·4	1	72·30	437·4
1	82·17	603·1	1	74·71	472·8
1	86·11	679·6	3	78·13	530·6
1	88·04	720·3	1	80·52	570·6
1	89·81	760·2	3	83·79	631·9
			1	87·64	709·9
			1	89·66	754·8

The two curves are in this case almost identical. A satisfactory equation has not yet been obtained owing to the absence of any measurements at low temperatures.

In the following Table the densities are compared at those temperatures at which the vapour-tensions are equal :—

Vapour-tension in millims.	Boiling-point of normal propyl iodide.	Boiling-point of iso-propyl iodide.	Density of normal propyl iodide.	Density of iso-propyl iodide.	Difference between densities.
200	62·37	50·50	1·66704	1·64590	0·02114
300	73·51	61·33	1·64493	1·62359	0·02134
400	81·95	69·70	1·62808	1·60646	0·02162
500	88·84	76·44	1·61446	1·59246	0·02200
600	94·70	82·11	1·60250	1·58068	0·02182
700	99·83	87·13	1·59221	1·57035	0·02186
760	102·63	89·86	1·58670	1·56497	0·02196

The above numbers show that the relation between vapour-tension and expansion, which had been rendered probable by Kopp's researches, does not exist, that the molecular volumes of the two isomers at corresponding temperatures are unequal, that of the normal iodide being greater than that of the other by an almost constant quantity. This fact is in accordance with the modern dynamical hypotheses on the constitution of matter. Isopropyl iodide is more unstable than the normal iodide; its instability may be due to the greater velocity of its molecules; from this greater velocity would follow a greater mean distance between the molecules.

I may here mention that I have made a very complete series of experiments on the vapour-tension of normal propyl alcohol. The curve representing these observations intersects that which expresses the tensions of normal propyl iodide, so that whereas at 760 millims. the iodide boils at 102°·5 and the alcohol at 97°·3, at 370 millims. they boil at the same temperature, viz. 79°·5, and at 120 millims. the boiling-point of the iodide is only 49°·5, whilst that of the alcohol is 56°.

This fact, which probably arises from the much greater latent heat of propyl alcohol, obviously renders useless all attempts to derive the boiling-points from the constitution of chemical compounds, so long as the boiling-points at the ordinary pressure of the atmosphere alone are taken into account.

Fig. 1.



Fig. 2.

